Precision Measurement of Time-Reversal Symmetry Violation with Laser-Cooled Polyatomic Molecules

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Precision searches for time-reversal symmetry violating interactions in polar molecules are extremely sensitive probes of high energy physics beyond the standard model. To extend the reach of these probes into the PeV regime, long coherence times and large count rates are necessary. Recent advances in laser cooling of polar molecules offer one important tool—optical trapping. However, the types of molecules that have been laser cooled so far do not have the highly desirable combination of features for new physics searches, such as the ability to fully polarize and the existence of internal comagnetometer states. We show that by utilizing the internal degrees of freedom present only in molecules with at least three atoms, these features can be attained simultaneously with molecules that have simple structure and are amenable to laser cooling and trapping.

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Precision measurements of heavy atomic and molecular systems have proven to be a powerful probe of high energy scales in the search for new physics beyond the standard model (BSM) [1]. For example, the limit on the electron's electric dipole moment (EDM), set by the ACME Collaboration using ThO, is sensitive to T-violating BSM physics at the $\gtrsim$TeV scale [2]. This sensitivity relies on the ability to experimentally access the large effective electromagnetic fields (>10 GV/cm) present in heavy polar molecules by fully polarizing them in the laboratory frame. This makes the experimental challenges of working with such a complex species worth the effort.

Despite the success of ACME, a current limitation of that experiment and all present molecular beam experiments is that their coherence time is limited to a few milliseconds by the beam transit time through an apparatus of reasonable size. Since EDM sensitivity scales linearly with coherence time, trapping neutral molecules has the potential to increase sensitivity by many orders of magnitude. Trapped molecular ions have shown great power in EDM searches [3], primarily due to their long coherence time of $\sim$1 s. Neutral species offer the ability to increase the number of trapped molecules much more easily and essentially without limit compared to ions, while retaining strong robustness against systematic errors. Here we show that laser-cooled and trapped polyatomic molecules offer a combination of features not available in other systems, including long lifetimes, robustness against systematic errors, and scalability, and present a feasible approach to access PeV-scale BSM physics.

A very promising route to trapping EDM-sensitive molecules is direct laser cooling and trapping from cryogenic buffer gas beams (CBGBs), which has advanced tremendously in the last few years [4–11]. The molecules that have been cooled so far posses an electronic structure that makes them amenable to laser cooling, but also precludes the existence of Ω doublets, such as the $^3\Delta_1$ molecular state used in the two most sensitive electron EDM measurements [2,3]. These doublets enable full polarization and "internal comagnetometry," which allows for the reversal of the EDM interaction without changing any lab fields. These features afford crucial robustness to systematic effects, especially as sensitivity continues to improve. There are a number of diatomic molecules with good sensitivity to BSM physics that are laser coolable, such as BaF [12], RaF [13], and YbF [14], though these molecules do not have closely spaced levels of opposite parity. They therefore require large and technically challenging lab electric fields $\gtrsim$10 kV/cm in order to be sensitive to the EDM, cannot be fully polarized, and do not admit internal comagnetometers—all of which leave them vulnerable to challenging systematic effects. Combining the requirement of laser cooling with the requirement of full polarization and internal comagnetometers eliminates all known choices of diatomic molecules. RaOH, a laser-coolable polyatomic molecule with BSM physics sensitivity, was previously considered for a precision measurement in the ground vibrational state [15], meaning that it would still suffer from the same drawbacks as diatomics.

We show here that low-lying excited vibrational modes in polyatomic molecules, which have not been previously considered for precision measurements, allow full polarization and internal comagnetometry via generic degrees of freedom, and are excellent candidates for a new class of precision measurements. Degenerate bending modes in these states give rise to lab-accessible angular momentum with a projection along the molecular dipole, enabling full polarization in small fields analogous to Ω doublets. However, unlike in Ω doublets these degrees of freedom are not coupled to the electronic spin and therefore do not

interfere with either laser-cooling properties or sensitivity to BSM physics. These structures are generic, and can be used to access these advantages with any atom that is sensitive to BSM physics.

The molecules we consider consist of an alkaline earth (or alkaline earth-like) atom monovalently and ionically bonded to some functional group. However, the ideas discussed are generally applicable to other polyatomic species. We show that these molecules have the significant additional advantage of being laser coolable, as was recently demonstrated with the polyatomic molecule SrOH [16] and proposed for a number of other species [15,17,18]. The essential property is the nonbonding s electrons being removed from the bonding region by orbital hybridization [19], resulting in highly diagonal Franck-Condon factors (FCFs). This property is not strongly dependent on the type of functional group bound to the metal atom [17,18]. Thus, polyatomic molecules isoelectronic to suitable diatomic candidates for fundamental physics searches such as BaF, YbF, HgF, and RaF have promise for laser cooling. Since the BSM physics sensitivity also comes from the nonbonding electron, it is largely independent of the bonding partners [15]. Furthermore, these polyatomic molecules are readily created in molecular beams and have well-studied and understood spectra [19].

We consider linear and symmetric top molecules, starting with the simplest type of molecule with the required characteristics—a linear nonsymmetric triatomic molecule XYZ. There are three distinct vibrational modes in this molecule [20]: X-Y stretch, bend, and Y-Z stretch, denoted by vibrational quantum numbers (ν_1, ν_2, ν_3), respectively. The ν_2 mode is doubly degenerate, as the bending can occur in two perpendicular directions. Since the molecule is symmetric about its axis, the eigenstates are sums of these two motions and the molecule has angular momentum ℓ along its symmetry axis, as shown in Fig. 1. In the excited $\nu_2 = 1$ mode, there are two such states with $\ell = \pm 1$, denoted $|\nu_2^{\pm\ell}\rangle$. Analogous to Ω doubling, Coriolis interactions lift the degeneracy between the even and odd parity states $|1^{+1}\rangle \pm |1^{-1}\rangle$, resulting in a parity doublet of size $q \sim O(B_e^2/\omega_2)$, where B_e is the rotational constant and $\hbar\omega_2$ is the vibrational energy for this mode [23]. For the types of species we consider this splitting is typically $\sim$10 MHz, and can therefore be mixed in moderate lab fields of $\sim$100 V/cm. The resulting polarized states are suitable to search for T-violating physics, and are such a generic feature that we can find them for polyatomics with any desired heavy atom.

As a specific example, we consider an electron EDM search in YbOH. We choose this molecule as our example case because it is readily created in a molecular beam, has been studied spectroscopically [26,27], is sensitive to many T-violating effects such as the electron EDM [28] and nuclear magnetic quadrupole moment [29] via the heavy Yb atom, and is a suitable candidate for direct laser cooling as we describe later. We stress again that the presented

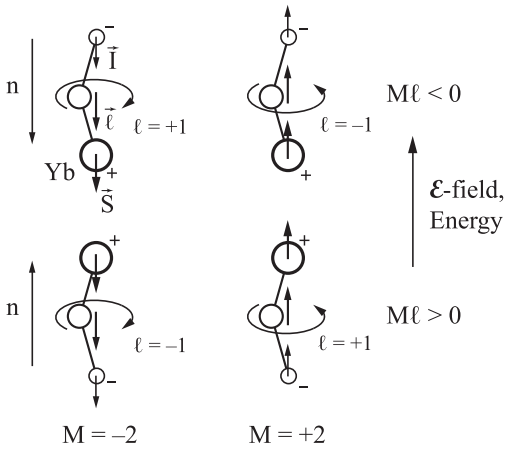

FIG. 1. Angular momentum in the fully polarized stretched states $F = |M| = 2$, in which each of the component angular momenta are stretched as well. The quantum numbers S, ℓ, and I are indicated at the top left. The internuclear axis points from the negative to the positive ion, meaning that the dipole moment lies along the internuclear axis. Compare the very similar figure for a $^3\Delta_1$ state like WC X [24] or ThO H [25]. Like Ω, ℓ is quantized in the molecule frame, which is why the direction of the vector $\vec{\ell}$ on the figure and the value of ℓ may differ. Since the EDM shift is $\propto \vec{S}\cdot n \propto \ell$, we can see that this interaction is reversed between the upper and lower Stark shifted states.

results do not depend on the specific properties of YbOH, and are quite generic. This molecule has a $^2\Sigma$ electronic ground state arising from a Yb-centered electron spin $S = 1/2$. S couples to the combined, total rotational and vibrational angular momentum N via spin rotation $\gamma N\cdot S$ to form $J = N + S$. The H nucleus has spin $I = 1/2$, which couples to J via Fermi contact $bS\cdot I$ to form the total angular momentum $F = J + I$, with projection M on the lab z axis. A schematic of these angular momenta is shown in Fig. 1, and the structure is discussed further in Supplemental Material. This is highly analogous to similar $^2\Sigma$ electronic states in diatomic molecules, with the important difference that N includes ℓ, a quantum number absent in diatomics.

Consider the $\nu_2 = 1$ state, which lies above the absolute ground state by about 300 cm$^{-1} \approx 10$ THz, and has an ℓ-doubling constant of $q \approx -10$ MHz, a spin-rotation constant $\gamma \approx 30$ MHz, and a hyperfine constant $b \approx 2$ MHz. The lifetime of this low-lying state is estimated to be $\gtrsim$10 s in Supplemental Material. To prove that this state is a good candidate for an EDM search, we examine its Stark, Zeeman, and EDM shifts.

Consider an electric field $\mathcal{E}$ applied along the lab z axis, and assume a (typical) dipole moment of $d = 4$ D, which saturates to a Stark shift of 1 MHz/(V/cm). This means that the dipole moment in these units is also the signed polarization, both of which are shown in Fig. 2. These levels were calculated by diagonalizing the $N = 1$ states including the Stark, spin-rotation, Fermi contact hyperfine, and ℓ-doubling interactions as described in Supplemental

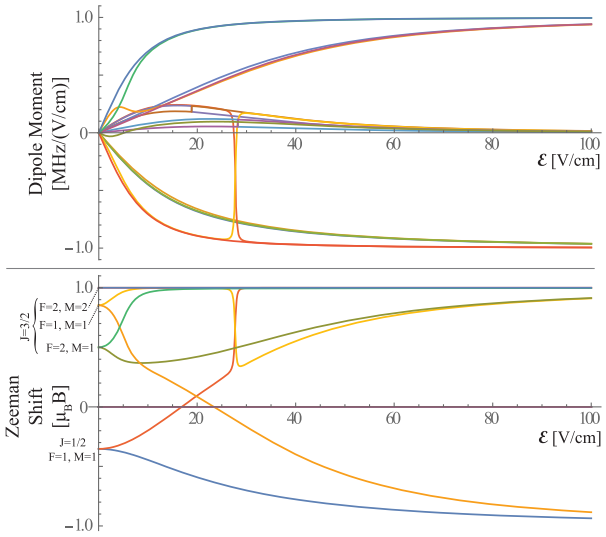

FIG. 2. Electric dipole moments (top) and Zeeman shifts (bottom) with $\gamma = 30$ MHz, $q = -10$ MHz, $b = 2$ MHz, and $d = 4$ D, representative of YbOH. The Zeeman shift is in units of $\mu_B \mathcal{B}$ in a small magnetic field. The dipole moment is also signed polarization, as described in the text. The jumps indicate avoided crossings. The labels on the left side correspond to the zero-field eigenstates. The colors in both plots correspond to the same states.

Material. We consider $\mathcal{E}$ small enough to neglect contributions from $N = 2$.

YbOH has states with >90% polarization at fields of ~40 V/cm, and >99.9% at 250 V/cm. Since the EDM shift is proportional to the polarization, this means that we can easily saturate the EDM sensitivity in the lab frame. The states with the largest polarizability are the stretched $F = |M| = 2$ states, which admit a simple intuitive diagram of angular momentum orientation, shown in Fig. 1.

We now consider a small magnetic field $\mathcal{B}$ parallel to $\mathcal{E}$, and calculate the combined Stark and Zeeman shifts. Figure 1 suggests that these polarized states have a linear Zeeman shift (electron spin either aligned or antialigned with $\mathcal{B}$ depending on the sign of M), which is confirmed by diagonalizing the full Hamiltonian (see Supplemental Material). The Zeeman shifts in a small magnetic field as a function of applied electric field are shown in Fig. 2.

There are electric fields where the effective g factors cross 0. Unlike cases where this has been considered previously [30–32], these fields are quite small. Unfortunately these states should have little EDM sensitivity; zero g factor means that the electron is not oriented in the lab, and since there is no strong coupling of the electron spin to the molecular internal frame, the electron cannot be aligned in the molecule frame either. However, these states could be very useful for systematic checks of $\mathcal{E}$-field dependence of spin precession without a background signal due to the much larger Zeeman effect.

Now consider the sensitivity to the electron EDM. Both S and $\hat{n} \equiv \mathrm{sgn}(M\ell)$ (the molecule dipole moment orientation) are stretched and aligned along the lab z axis, so the EDM shift in the polarized limit is simply given by $\Delta_{\mathrm{EDM}} \propto S{\cdot}n \propto \mathrm{sgn}(S{\cdot}z)\mathrm{sgn}(n{\cdot}z) = \ell$, perfectly analogous to the shift $\Delta_{\mathrm{EDM}} \propto \Omega$ for a fully polarized diatomic molecule in a state with Ω doublets. The EDM shift reverses sign upon changing the molecule orientation, which provides the desired internal comagnetometer via spectroscopic reversal.

The stretched states have the simplest interpretation, but other states are equally useful. In particular, for both the Stark and Zeeman effects all of the states saturate to either the same absolute value, or 0. For the Stark effect, this is simple to understand; only N has any interaction with the applied field to first order, so $N = 1$ should have at most three values of dipole moment in the fully polarized limit. The Zeeman shift saturates as a result of the applied electric field decoupling the molecular dipole moment and symmetry axis from the electron spin and occurs when $|d\mathcal{E}| \gtrsim |\gamma|$, analogous to the decoupling of atomic electron and nuclear spins in a high magnetic field. The symmetry axis and electron spin are aligned in the lab for any Stark-shifted state with $M \neq 0$, meaning that the EDM sensitivity saturates to the same value for any pair of $\pm M$ states in the Stark-shifted manifolds. This means that we can use any pair of $\pm M \neq 0$ states (with the same Stark shift) to perform the measurement, eliminating the need for potentially difficult coherent preparation of states with large angular momentum projection difference. Note that all such states have > 99% polarization in a 300 V/cm field.

Now we discuss how these molecules can be laser cooled, and show that it can be performed efficiently. This is a necessary step for loading a magneto-optical trap (MOT), which is a very promising step in the path to trapping with long coherence times. Laser cooling and trapping of YbOH is feasible using the scheme originally proposed for CaOH [17] and experimentally demonstrated with SrOH [16]. Like SrOH, YbOH is an ionic molecule with the two lowest electronic states $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ originating primarily from $4f^{14}6s\sigma$ and $4f^{14}6p\pi$ Yb^+ atomic orbitals, respectively. Figure 3 shows the main $\tilde{X}^2\Sigma^+(000) \leftrightarrow \tilde{A}^2\Pi_{1/2}(000)$ laser-cooling transition λ_0 as well as the dominant off-diagonal vibrational decay channels in the Born-Oppenheimer (BO) approximation with FCFs $f \gtrsim 0.001$. Similar to its electronic analogue YbF [14], the FCFs are quite diagonal. With four repumping lasers λ_{1-4}, shown in Fig. 3, we can scatter thousands of photons. This allows for transverse beam compression via the Doppler force leading to at least an order of magnitude enhancement in on-axis peak beam density [33], directly resulting in enhanced MOT loading [34]. Efficient one-dimensional Sisyphus laser cooling of triatomic molecules has been demonstrated with only a few hundred photons [16] and upon two-dimensional implementation in YbOH will lead to ×6 increased flux for MOT loading. Scattering of $\gtrsim 10^4$ photons per molecule should be possible with five

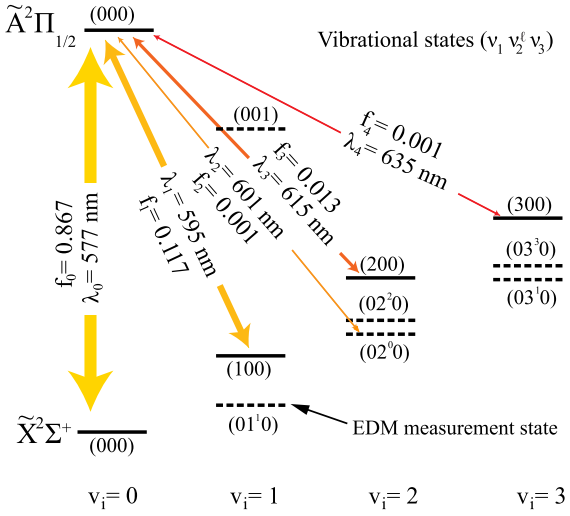

FIG. 3. Proposed photon cycling and laser-cooling scheme for YbOH. Thicker lines indicate stronger transitions with appropriate Franck-Condon factors (f) and wavelengths (λ) indicated. The energy splittings are not to scale.

vibrational repumpers, enabling longitudinal slowing [35] and direct magneto-optical trapping [7].

CBGBs can be used to produce high brightness and low velocity beams of nearly any small molecule [36]. Many molecules of the type under consideration, for example YbOH [26] and YbCCH [37], have been created in beams by ablating metal into an inert carrier gas mixed with a reactive gas like H_2O_2 and HCCH, respectively, a technique commonly implemented in CBGBs as well.

While excited bending vibrations are populated during the laser ablation process [38], they quench relatively quickly through inelastic collisions with helium buffer gas [39]. A CBGB of YbOH would mostly include molecules in the lowest vibrational state (000), and require pumping into the excited bending mode. This pumping can be achieved via the excited $\tilde{A}(010)\mu^2\Sigma^{(+)}$ state, as discussed in Supplemental Material.

Linear triatomic molecules are the easiest to understand, but slightly more complex molecules offer a possible advantage. In particular, for symmetric top molecules the K doublet is analogous to the ℓ doublet, where K is the projection of the total rotational, orbital, and vibrational angular momentum on the symmetry axis [21]. The advantageous features of ℓ doublets are preserved, as is the ability to laser cool species such as $YbCH_3$ and $YbOCH_3$ [17,18]. However, K-doublet splittings are even smaller, typically $\lesssim$kHz, meaning that complete polarization requires only $\lesssim$1 V/cm electric fields, and the excited K levels are even closer to the ground state (typically $\sim$100 GHz). Other molecular structures may reveal additional advantages.

ℓ and K doublets are quite generic and not limited to monovalent alkaline earths. Species such as RaOH [15], RaCO, RaNC, TlOH, ThCH, LuCH, PbOH, HfCH, LuCO, and many more (both diamagnetic and paramagnetic) can be used to search for a wide array of BSM physics beyond the electron EDM, including nuclear magnetic quadrupole moments, nuclear EDMs, nuclear Schiff moments, parity violation, and so on. Some of these molecules may not be as readily laser cooled, though we could potentially create "custom" species with a laser-coolable atom, for example, TaCOCa. Such species also have the potential for optical-cycling readout on the "BSM physics atom" via coupling of different spin polarizations to various internal states involving the laser-cooling atom. Combining such laser-coolable centers would be advantageous even for species that can be laser cooled directly; a molecule such as YbCCCa would offer increased scattering rates and optical forces, and even more internal comagnetometry. Since both YbCCH and CaCCH can be created in a beam by reactions of the metals with HCCH [37,40], there is a promising path to creating such molecules. We can also consider molecules for ion trap experiments, where the internal comagnetometers are necessary [3] since there is no ability to reverse the applied electric field, such as $LuOH^+$ or $RaOH^+$. Additionally, the combination of laser cooling, optical readout, and linear Stark shifts in small fields could be useful for quantum information processing and quantum simulation [41,42].

As an example of what sort of gains are to be had with this approach, consider 10^6 trapped molecules [11] with 10 second coherence time [43,44], 50% combined preparation and detection efficiency, and one week of operation. Such an experiment would increase sensitivity to the electron EDM by 4 orders of magnitude above the current limit, reaching into the PeV regime [2,45].

In conclusion, we have analyzed an experimentally viable approach for measuring T-violating interactions with simple polyatomic molecules in order to search for BSM physics at the PeV scale. Linear and symmetric top molecules containing a heavy metal atom like Yb provide a robust platform for an EDM search via laser cooling and trapping, and are the first system to combine the primary advantages of the competing approaches. Supplemental Material can be found in Ref. [46] and includes additional Refs. [47–69].

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